

# Journal Pre-proof

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PII: S2238-7854(21)00026-0

DOI: <https://doi.org/10.1016/j.jmrt.2021.01.025>

Reference: JMRTEC 2640

To appear in: *Journal of Materials Research and Technology*

Received Date: 15 October 2020

Revised Date: 9 January 2021

Accepted Date: 10 January 2021

Please cite this article as: Mustapha AN, Zhang Y, Zhang Z, Ding Y, Yuan Q, Li Y, Taguchi and ANOVA analysis for the optimization of the microencapsulation of a volatile phase change material, *Journal of Materials Research and Technology*, <https://doi.org/10.1016/j.jmrt.2021.01.025>.

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# Taguchi and ANOVA analysis for the optimization of the microencapsulation of a volatile phase change material

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Keywords: ANOVA analysis, Taguchi, Microencapsulation, Volatile organic compounds,  
Phase change materials, Process optimization

**Abstract**

The microencapsulation of volatile phase change materials is an important and challenging area for low-temperature thermal energy storage. Our previous studies have effectively addressed the challenge of long-term volatile core retention and also indicated that the quality of the obtained poly(urea-formaldehyde) microcapsules is highly affected by various process parameters, including reaction temperature, initial pH, reaction time, and homogenization speed. In this paper, the Taguchi orthogonal array has been employed to optimise controllable process parameters to identify the most synergistic combination, in order to maximise the payload, yield, and encapsulation efficiency. The Taguchi signal-to-noise ratio results substantiated that the most efficient combination of parameters was 3 hours reaction time, pH 3.5, 55 °C reaction temperature, and 1200 rpm homogenization speed. With this combination of parameters, microcapsules with superbly high payload of 95.2 %, as well as a yield of 30.5 % and encapsulation efficiency of 71.1 % were amalgamated. In addition, Analysis of Variance (ANOVA) was also utilised to demonstrate the mean response magnitudes (% contribution) of each of the four controllable process parameters, in terms of contribution for the payload, yield, and encapsulation efficiency. Overall, it was indicated that the temperature is the most influential parameter at 83.1 % contribution, followed by pH at 6.8 %, reaction time at 5.2 %, and homogenization speed at 4.9 %. Such findings in this work postulate the fundamental insights into maximising the output of the formulation conditions, which in turn is aimed to minimise the time and cost of production of the microcapsules.

## 1. Introduction

Phase change materials (PCMs) are an auspicious group of materials that are prodigious for their use in thermal energy storage (TES) applications. As PCMs undergo phase changes, thermal energy is released at nearly constant temperatures. These assembly of materials are alluring due to their high energy storage density over a small temperature range [1]. PCMs are pertinent for their use in thermal regulation applications where there are periodic heat input/dissipation and intermittent energy supplies [2]. However, employing PCMs in a traditional manner without any protective medium emanates the inconvenience of increased associated costs, such as specific heat exchange surfaces, latent heat devices, metal matrices [3–8].

PCMs can be encapsulated by an inert wall material to circumvent the issue of leakage in unit operations. There has been an abundant array of researchers that have encapsulated PCMs, notably Brown et al. [9]. Microcapsules with a rough outer surface were bequeathed, with a smooth inner membrane, as is a common feature in many microencapsulation studies [9–12]. Substantial attention is concerted on the encapsulation of PCMs with melting points ranging from  $-10$  to  $80$  °C, many of which are employed for energy storage applications, and for use in building envelopes [13–18]. Some research has been conducted recently on the microencapsulation of low melting temperature volatile PCMs, such as heptane [19–21] for their potential applications in cryogenic processes. Volatile PCMs are more challenging to encapsulate due to higher vapour pressures, resulting in difficulty in encompassing the core material during storage or employment in extreme temperature ranges. For example, at  $20$  °C heptane has a vapour pressure of  $\sim 5.3$  kPa, whereas dicyclopentadiene has a vapour pressure of  $\sim 0.18$  kPa, rendering heptane a more difficult core material to contain in the microcapsule for extended time periods.

The microencapsulation process relies on multiple controllable and uncontrollable formulation process parameters, which interrelate in a synergistic manner [13]. The optimal combination of key controllable parameters is pivotal for the overall process, in terms of increasing production output, process efficiency, reducing energy consumption, as well as decreasing the effects of uncontrollable parameters. Due to the capacious variables that are involved in the encapsulation process, it can be an arduous task to assign the individual outcome of specific parameters [22]. Conventionally, optimization studies involve the variation of one controllable parameter, while other controllable parameters remain constant. However, this is a very strenuous technique that can be both time consuming and expensive [23]. In order to determine the optimal conditions for the formulation of the microcapsules to gain high payload and encapsulation efficiency, a time-efficient orthogonal factorial design method known as the ‘Taguchi’ method was utilised instead in this paper as it offers the advantage of optimizing the process with fewer required experimental procedures [24]. The ‘Taguchi’ method is a robust systematic experimental design technique to minimize uncontrollable factors [24–26] and has been widely used in an array of fields such as the optimization of drilling parameters in the drilling of steel [25] and the parametric study of epoxy loaded PMMA microcapsules [24]. The Taguchi method is a powerful tool to identify the optimal combination of process parameters in order to reduce the cost, improve the quality, and/or increase the efficiency.

In conjunction with the ‘Taguchi’ technique, the Analysis of Variance (ANOVA) method is an established method that is utilised to verify the percentage contribution of each process parameter on the desired outputs. In particular, the parametric studies have been carried out on PCM microcapsules with less volatile core materials, such as PMMA [24], paraffin wax [27], hexadecane [28] and lauric acid [29]. The recent advancement in the retention of volatile organic compounds for low temperature energy storage applications inflates the requirement

of optimising process conditions for the successful and efficient core encapsulation [19]. In this paper, experimental work on the microencapsulation of volatile PCMs has been conducted firstly to find the optimal combination of formulation parameters (including reaction time, pH, homogenization speed and reaction temperature) using the Taguchi technique, and then to examine the contribution of these parameters using the ANOVA method. The overall goal is to identify the optimal controllable process parameter values and also which parameters need to be precisely controlled while maintaining reasonably high payload, yield, and encapsulation efficiency for potential scale-up manufacturing.

## 2. Experimental Procedure

For the following section, heptane was used as the core material, to be encapsulated with urea and formaldehyde, via the one step in situ polymerization approach. During the formulation process, each component was weighed, in order to calculate the payload, encapsulation efficiency and the yield of the microcapsules. Optical microscopy was utilised to observe the microcapsule morphology and core material retention, while scanning electron microscopy was used to further characterize the morphology, shell roughness and shell thickness of the microcapsules. Further characterization was carried out with a mastersizer to measure the size distribution.

### 2.1. Microcapsule formulation

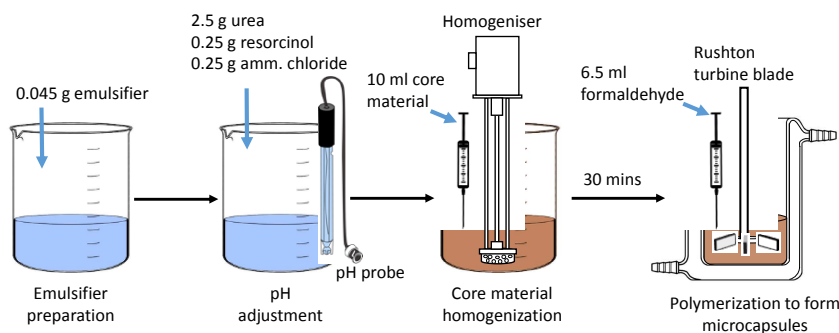


Figure 1. The one step in situ polymerization process for the formulation of poly(urea-formaldehyde) (PUF) microcapsules.

The following chemicals and materials were purchased from Sigma-Aldrich (UK): Heptane (246654, anhydrous, 99%), urea (U5128, ACS reagent grade 99.0-100.5%), formaldehyde solution (47608, for molecular biology, BioReagent,  $\geq 36.0$  % in H<sub>2</sub>O), Nile red (72485, for microscopy), gelatin (04055, from porcine skin), resorcinol (398047,  $\geq 99.0$  %). Ammonium chloride (RC-015) was purchased from G-biosciences (UK). Unless otherwise stated or specified, all the materials from the suppliers were used without further modification or purification.

Figure 1 illustrates the formulation process. The emulsifier solutions were prepared prior to the experiment, by mixing gelatin in 150 g of distilled water to make a gelatin concentration of 0.03 wt%. It was ensured that the gelatin emulsifier fully dissolved in the water before the reaction proceeded. Using a Sartorius Secura 124-IS analytical balance, 2.5000 g urea, 0.2500 g ammonium chloride, and 0.2500 g resorcinol were measured into the previously prepared 150 ml beaker, with an acceptance of (+/-) 0.0005 g. Using an IKA RCT magnetic stirrer, the solution was stirred until it was completely clear. Subsequently, the pH was measured using a Mettler Toledo FiveEasy pH meter and was further adjusted to the required value by adding dropwise 1 molL<sup>-1</sup> HCl solution or NaOH solution when necessary. The pH was left to stabilize for 5 minutes.

During the stabilization period, the core material was prepared. Nile red was dissolved in 10 mL heptane via ultra-sonification for 5 minutes, to be used as a non-destructive core material retention indicator, based on the method proposed by Zhang et al. [21]. After the 5 minutes of pH stabilization, the 150 mL beaker was then placed under a Silverson L5M homogenizer under fume hood conditions. The homogenization was initiated, and the core material was injected into the 150 ml solution via a 10 mL syringe. This was left for 20 minutes to fully disperse the core material into the solution.

Successively, 6.5 mL of formaldehyde was measured into a 10 mL syringe. After the 20 minutes proceeded, the homogenised solution was transferred into a 250 mL jacketed beaker, which included 4 stainless steel baffles of standard configuration to stimulate mixing. This was connected to a Julabo ME-F25 water bath. A Rushton turbine agitator blade (IKA R3004 30 mm diameter) connected to an IKA MINISTAR 20 Control Mixer was used to keep the emulsion stabilized, with a stirring speed of 600 rpm. The formaldehyde was injected into the jacketed beaker, and the program was set on the water bath to initiate the reaction. The program consisted of the temperature being maintained at 20 °C for 30 mins, and then at a rate of 1 °C/min, the temperature was raised to the required reaction temperature. The temperature was held at the set temperature for the duration of the reaction time, and then cooled down to 20 °C at a rate of 1 °C/min. This formulation was proved to be effective, as observed in our previous publications [19,21].

After the reaction completed, the products were centrifuged 4 times at 5000 rpm (relative centrifugal force (RCF) of 3480 ) with a Labnet Z-306 Hermle Universal Centrifuge, for 5 minutes each time. A vacuum filter was then used to wash the samples, with 5 L of warm water. Once the capsules were formulated, they were re-dispersed in distilled water and kept in centrifuge tubes, which could then be dried and used for further characterization when needed.

## 2.2. Post-formulation observation

The optical images of the microcapsules were obtained from a Leica DMRBE microscope, straight after the formulation process and 24 hours after drying the microcapsules in air, to observe the core material retention. As Nile red was dispersed into the core material, the emission spectra of the Nile red were gathered with a CoolLED pE-300 SB LEDs illumination system, which was fitted onto the microscope, with an excitation wavelength of



460 nm. In this case, Nile red can be used as a core material indicator, employing the principle of solvatochromism [19,21,30]. A bright green colour emitted from the microcapsules would indicate core material retention, whereas a red colour would indicate loss of core material.

The morphology and shell thickness of the microcapsules were characterized with a Hitachi TM3030Plus Tabletop SEM. Prior to the SEM investigation, the capsules were coated with 5 nm of gold using a Quorum Q150R ES gold sputter, utilising argon as the inert gas, with a pressure of 0.5 bar. The size distributions of the microcapsules and the evolution of the polymer shell material size over time were examined using a Malvern Mastersizer 2000 Particle Size Analyzer with a wet dispersion unit (Hydro 2000S). Distilled water was used as the dispersant. The obtained shell thickness and size distributions were used to assist the parameter range selection for further 'Taguchi' and ANOVA analysis and also to validate the quality of the formulated microcapsules.

### 2.3. Payload, yield and encapsulation efficiency

To characterize the payload of the microcapsules, the dried samples were weighed and then compressed with a Lloyd X Materials Testing Machine. A maximum force of 80 kN at 10 mm/min for 120 s was used to compress the microcapsules to breakage, to release the heptane. Successively, the capsules were left to dry in a fume hood for a duration of 4 hours for further evaporation of the heptane. The dry capsule shells were then weighed. The payload of the formulated microcapsules (PL) which is the mass ratio of the core materials to the microcapsules was calculated by:

$$PL = 1 - \frac{w_{dc}}{w_d} \quad (1)$$

where  $w_{dc}$  is the weight of the compressed capsule shells, and  $w_d$  is the weight of the uncompressed dried microcapsules.

The yield of the formulation process which is the mass ratio of the product to raw materials was then calculated by:

$$\text{Yield} = \frac{w_t}{w_{Rtot}} \quad (2)$$

where  $w_t$  is the total mass of the formulated dry microcapsules, and  $w_{Rtot}$  is the weight of all the materials used for synthesizing the shell and core, excluding the water.

The encapsulation efficiency (EE) which is the percentage of encapsulated core materials was then calculated by:

$$\text{EE} = \frac{W_T \times PL}{\text{Hep}_{in}} \quad (3)$$

where  $\text{Hep}_{in}$  is the total amount of heptane supplied for the homogenization process.

#### 2.4. Thermal Cycling

Thermal cycling for the microcapsules was carried out using a TA Instruments DIL 806 Dilatometer, incorporated with a liquid nitrogen dewar and a PolyScience water bath.

Ultrathin double-sided tape (Tesa 68,557 ultrathin PET tape) was placed on a glass slide, and the microcapsules were placed on top. The microcapsules were observed under FM before and the cycling, with a precise marked location. 10 cycles were then performed with 25 L of liquid nitrogen from 25 °C to -140 °C, at a heating/cooling rate of 7.5 °C/min. The samples were then observed in the same location after cycling under FM, for comparison of the integrity and core material retention.

## 2.5. Differential Scanning Calorimetry

A Mettler Toledo DSC 3 was used to observe the phase transition of the MPCMs, with liquid nitrogen employed as the coolant. The N<sub>2</sub> gas flow was set at 20 mL/min, and the cooling/heating rates were 5 °C/min. The microcapsules were sealed inside 40 µL aluminium crucibles. The temperature profile was set to cool down from –60 °C to –140 °C, then isothermally maintaining this temperature for 5 minutes, and then heating back up to 60 °C, all at a rate of 5 °C/min.

## 3. Results and Discussion

### 3.1. Process parameter selection

In this study, various process parameters can be selected to be optimized, in order to maximise the yield, payload and/or encapsulation efficiency. Nguon et al. [13] discussed the various variables that can be manipulated to target various determining parameters. For example, to optimize yield, previous studies variables that were optimized included core/shell ratio, reaction time, homogenization speed, initial pH, and the heating rate [13]. For the payload, parameters such as reaction temperature, homogenization rate, reaction time and core/shell ratios were deliberated [13]. In our process, the payload as well as the encapsulation efficiency are the key optimal targets while the yield is a secondary indicator. As compact shell is required to retain the highly volatile core material, a constant and low core/shell ratio was selected based on our preceding experience [19–21]. As a result, we select the reaction time, reaction temperature, pH value and the homogenization speed as the process controllable parameters and we have carried out the process variable screening experiments prior to the Taguchi orthogonal array experiments to identify the range of these parameters.

#### 3.1.1. Reaction Time

To preliminarily explore the effect of time on the reaction progression, a batch was made at pH 3.5 and 55 °C, consisting of the reactive substituents without the heptane core material, to examine the size growth of the shell polymer particles over time. The experimental conditions were based on the method carried out by Brown et al. [9]. As shown by Figure 2, it seems that a rapid increase in the polymer size occurs from time 15 min to ~ 90 min and stabilises at ~ 120 minutes onwards. Therefore, a 3-hour reaction time was proposed as the minimum, followed by 4 hours, and 8 hours. A 2-hour batch (containing the heptane core) was initially formulated but there was immediate leakage of the heptane, as observed under the fluorescence microscope (FM), whereas a 3-hour batch survived the 24 hours of ambient drying, as shown in Figure 2 (b) and (c).

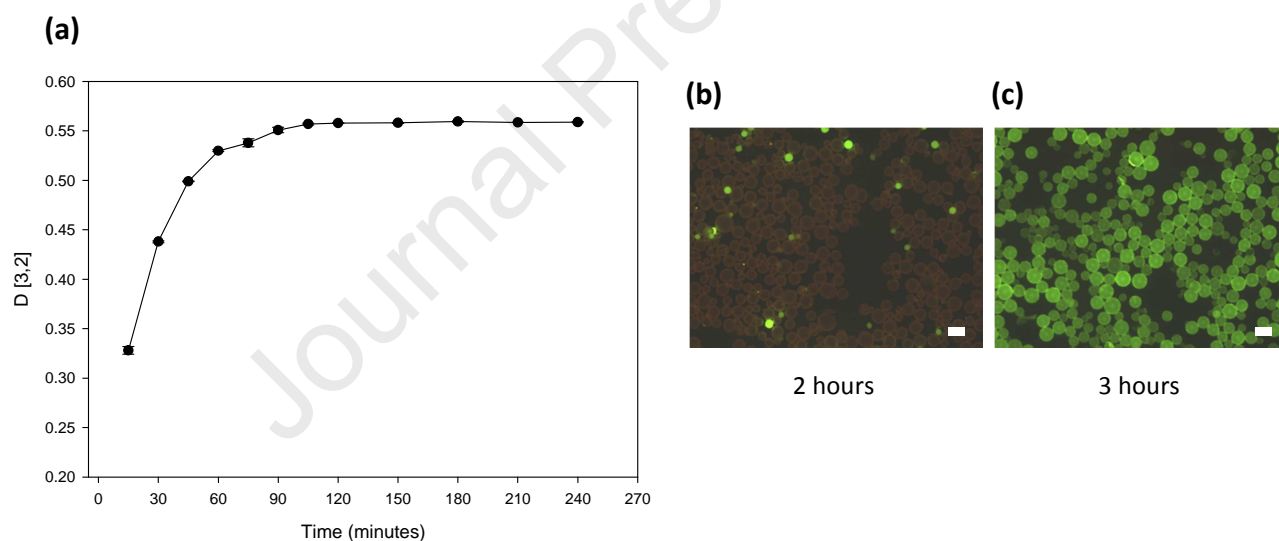


Figure 2. (a) Size growth profile of the shell particles over a duration of 4 hours; (b) 24-hour dried FM image of the microcapsules formulated over 2 hours; (c) 24-hour dried FM image of the microcapsules formulated over 3 hours (scale bars are 100 μm).

### 3.1.2. Reaction pH

As the in-situ polymerization reaction is dependent on the initial pH of the reaction, this was an essential factor to study. Methylol-ureas are low molecular weight pre-polymers that are formed in the initial stages of the encapsulation process. Higher pH values would result in higher amounts of methylol-ureas, leading to smoother samples. Lower pH values result in methylene and ether bridged compounds, resulting in rougher and potentially more porous shells [31], which may affect the payload and the long term retention of the core. However, it is important to note that the one-step in situ polymerization process can only occur in acidic pH, and there must be a limitation on how low the pH is set to bequeath smooth microcapsules. Rochmadi et al. [32] stated that in acidic conditions, the rate of condensation is higher, and provided a proposed reaction rate equation:

$$R_{uf} = k_r(C_{uf})^2 + k_c a(C_{uf} + C_{uf,s}) \quad (4)$$

where  $R_{uf}$  is the overall condensation reaction rate for the formation of urea-formaldehyde (UF) particles,  $k_r$  is rate constant,  $k_c a$  is the mass transfer coefficient,  $C_{uf}$  is the aqueous phase UF pre-polymer concentration,  $C_{uf,s}$  is the UF pre-polymer concentration on the microcapsule surface,  $k_r(C_{uf})^2$  is the rate of formation of the UF polymer micro/nanoparticles, and  $k_c a(C_{uf} + C_{uf,s})$  is the rate of formation of the microcapsule shell.

Rochmadi et al. [32] stated that the reaction rate constant,  $k_r$ , is proportional to the  $H^+$  concentration in the solution. Therefore, a very high  $H^+$  concentration in the solution (a low pH), results in a higher  $k_r$ , consequently promoting the rate of formation of branched UF particles at an accelerated manner. This is in agreement with the work carried out by Katoueizadeh et al. [33], who stated that at high pH values (above 7), the condensation reactions did not occur.

Wang et al. [34] investigated the effect of pH for the formulation of liquid poly sulphide with a UF shell, with a pH range of 2 to 4.5. It was observed that at pH 4.5, there was a deceleration of the polymerisation rate, while at pH 2, accelerated polymerization was observed, with increased surface roughness of the microcapsules due to participate formation.

To investigate the effect of pH, 3 batches were made, all with 3 hours reaction time, 55 °C and a homogenization speed of 1200 rpm. The initial pH values were altered, With values of 2.5, 3.5 and 4.5. It can be seen from the SEM micrographs on Figure 3 (a) that the pH 2.5 samples had a much rougher shell surface, with a larger proportion of UF microparticles. The sample with pH 4.5 yielded a much smoother profile, with smaller UF satellite nanoparticles present. Central areas of the image were selected and using ImageJ (an image processing programme) and MATLAB, the proportion of the smooth profile to the lighter satellite particles in terms of total area on the SEM micrographs were quantified, as seen on Figure 3 (b). With 5 images taken, the average proportion of satellite particles (SP) to the smoother membrane (M) was postulated. It was calculated that the pH 2.5 had a SP composition of 13.3 %, while pH 3.5 had 6.3 %, and pH 4.5 with 3.3 %. Therefore, in this work the pH range was selected to be 2.5-4.5.

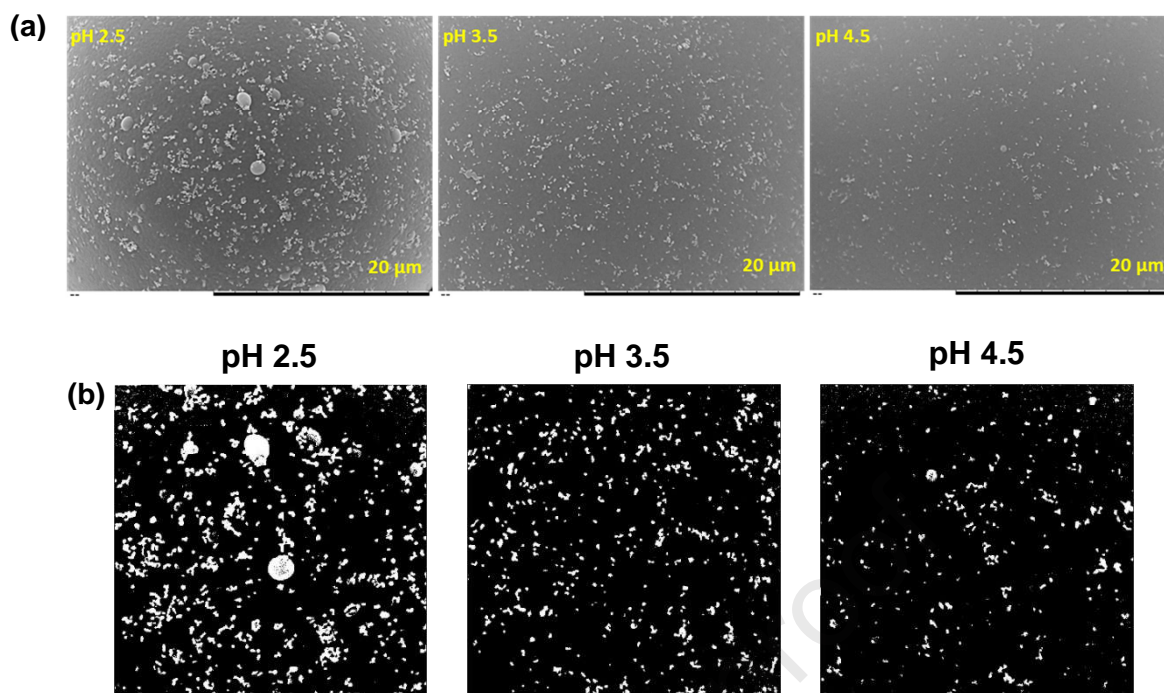


Figure 3. (a) SEM micrographs of the surface of individual microcapsules with various pH values made with the following reaction conditions: 3 h reaction time, 55 °C reaction temperature, 1200 rpm homogenization speed; (b) binary images of the SEM images for the increasing pH samples (binary images are all 650 pixels by 650 pixels).

### 3.1.3. Reaction temperature

The reaction temperature in the one step in situ polymerization process is also another important factor to study. The rate of UF polymer formation and microcapsule shell thickness is proposed to be determined by the pH and reaction temperature [13]. Fan and Zhou [35] proposed that the porosity of the outer shell layer is dependent on the rate of UF nanoparticle formation. Nguon et al. [13] propositioned that the rate of nanoparticle formation is dependent on the rate of polycondensation, which is also affected by the reaction temperature. For example, during the encapsulation of palm oil with a UF shell, an increase of the reaction temperature from 50 °C to 70 °C resulted in the increase of nanoparticle formation and resulted in a reduction of encapsulation efficiency by 80 % [32]. Furthermore, the encapsulation of liquid polysulphide with a UF shell at 80 °C resulted in very irregular microcapsules with poor core material retention and large precipitates [34]. Increasing the rate of polymer formation (by increasing the temperature), results in greater formations of

nanoprecipitates, shortening the deposition on the core surface [13]. However, a temperature that is too low is not enough to break the energy barrier required for the reaction. Cosco et al. [18] disclosed that during the encapsulation of epoxy with a UF shell at 60 °C and 40 °C, low reaction temperatures affected the encapsulation efficiency. To explore the effects that the reaction temperatures have on the encapsulation efficiency and payload, a range of 45 °C, 55 °C and 65 °C will be used for the Taguchi orthogonal array.

#### 3.1.4. Homogenization Speed

For the core material dispersion into the aqueous phase, a minimum shear rate is required for the mixing between the two immiscible phases. If this minimum shear rate is achieved, there is an inverse relationship between the size of the droplets, and the homogenization rate [18,48]. Depending on the shear rate, the morphology and size distribution of the microcapsules will vary. During the encapsulation of n-octadecane, Zhang et al. [36] observed an increase in diameter with a decrease in homogenization speed, as well as a smoother shell, leading to a higher payload. Dong et al. [37] also observed that an increase in the homogenization speed while encapsulating peppermint oil, led to multinuclear microcapsules with a lower oil content. There have been many studies in which the homogenization speed has been varied to study the effects on the microcapsules, many of which ranging from 400 rpm to 2000 rpm [9,16,29,35,37]. For this study, a range of 600 rpm, 1200 rpm and 1800 rpm were used.



### 3.2. Signal to noise (S/N) analysis for the microcapsule formulations

The Taguchi orthogonal array was utilized to identify the optimal process parameter combination. In this study, the controlled variables are altered in order to manipulate the noise factors (uncontrollable factors). These noise factors are external stimuli that are difficult to control, affecting the formulation process. Examples of these include ambient temperature, process equipment vibrations and environmental humidity. The identification and consequent exploitation of the optimal control factor settings is therefore the aim to enhance the formulation process.

From the results, the signal to noise ratio (S/N) can be calculated, in which the key control variables can be identified to reduce the noise factors [23–25]. In this study, the S/N ratios for each of the control factors were calculated, in order to maximise the payload, yield and encapsulation efficiency of the microencapsulation process. Depending on the goal of the experimental targets, there are three main cases of S/N ratios, as shown in Table 1. These three cases are termed as ‘nominal is best’, ‘larger is better’ and ‘smaller is better’ S/N values. Since this study is aimed to maximise the yield, payload and encapsulation efficiency, the S/N ratio targets to achieve that ‘the larger is better’ were used. The S/N values are calculated from experimental outputs, in which  $S$  is the signal value,  $N$  is the noise value,  $n$  is the number of experimental repetitions,  $y_i$  is the measured response value (payload, yield, or encapsulation efficiency). The S/N ratio values were used to quantitatively measure a response (e.g. the microcapsule payload) as a result of altering a parameter in the formulation process. As discussed in section 3.1, the four factors to be investigated include reaction time, pH, temperature and homogenization speed. Table 2 conveys the synthesis conditions utilized to prepare the microcapsules, all of which have 3 levels. Minitab, a statistical design software package, was utilised to design the Taguchi orthogonal array, as shown in Table 3.

Table 1. S/N ratio experimental goals and equations.

S/N Ratio	Experimental Goal	Ratio
Nominal is the best	Positive, zero or negative	$\left(\frac{S}{N}\right) = -10 \log \left( \frac{1}{n} \sum_{i=1}^n (y_i^2 - y_0^2) \right)$
Larger is better	Maximise the response	$\left(\frac{S}{N}\right) = -10 \log \left( \frac{1}{n} \sum_{i=1}^n \frac{1}{y_i^2} \right)$
Smaller is better	Minimising the response	$\left(\frac{S}{N}\right) = -10 \log \left( \frac{1}{n} \sum_{i=1}^n y_i^2 \right)$

Table 2. Selected reaction control factors and respective levels.

Level	Factor			
	Reaction time (h)	pH	Temp (°C)	Homog. Speed (rpm)
1	3	2.5	45	600
2	4	3.5	55	1200
3	8	4.5	65	1800

Table 3. Orthogonal array of process variables for optimization.

Run	Reaction time (h)	pH	Temp (°C)	Homog. speed (rpm)
1	3	2.5	45	600
2	3	3.5	55	1200
3	3	4.5	65	1800
4	4	2.5	55	1800
5	4	3.5	65	600
6	4	4.5	45	1200
7	8	2.5	65	1200
8	8	3.5	45	1800
9	8	4.5	55	600

Table 4. Taguchi orthogonal experimental results for the payload, yield, and encapsulation efficiency, as well as the respective calculated S/N values.

Run	Factors				Results					
	Time	pH	Temp	Homog. Speed (rpm)	PL (%)	S/N PL	Yield (%)	S/N Yield	EE (%)	S/N EE
1	3	2.5	45	600	30.5	34.5	11.8	26.2	5.9	20.2
2	3	3.5	55	1200	95.2	44.3	30.5	34.5	71.1	41.8
3	3	4.5	65	1800	87.3	43.6	28.6	33.9	61.7	40.6
4	4	2.5	55	1800	85.5	43.4	28.7	33.9	61.9	40.6
5	4	3.5	65	600	96.1	44.4	28.9	33.9	68.7	41.5
6	4	4.5	45	1200	15.2	28.4	13.8	27.6	5.3	19.3
7	8	2.5	65	1200	41.1	37.0	16.1	28.9	33.9	35.4
8	8	3.5	45	1800	24.2	32.4	12.3	26.6	7.4	22.2
9	8	4.5	55	600	95.3	44.4	28.7	33.9	67.4	41.3

The effects of the reaction factors on the payload, yield and encapsulation efficiency were collated and quantified, as displayed in Table 4. The experimental results were evaluated, and the corresponding S/N values were calculated. From primary observation, it is apparent that the lowest payloads were obtained for the samples produced at 45 °C, with 30.5% (S/N 34.5), 15.2 % (S/N 28.4) and 24.2 % (S/N 32.4) for reaction-set 1, 6 and 9 respectively. A similar trend is also observed for yield and encapsulation efficiency. To further explore this, OM and FM were utilised to observe the microcapsules.

Over a 24-hour period, the core material retention was studied, by utilising a fluorescence microscopy to study the Nile red preservation in the capsule. The bright green colour displays core material retention, whereas the dim or red colour indicates leakage or collapse. It is conveyed that in Figure 4, Figure 5, and Figure 6 all of the capsules produced at 45 °C had very poor retention, with the majority of the capsules collapsing over a 24-hour period. Furthermore, another batch that was produced at 65 °C, and the capsules also collapsed after 24 hours, as seen on image 7(C) on Figure 6.

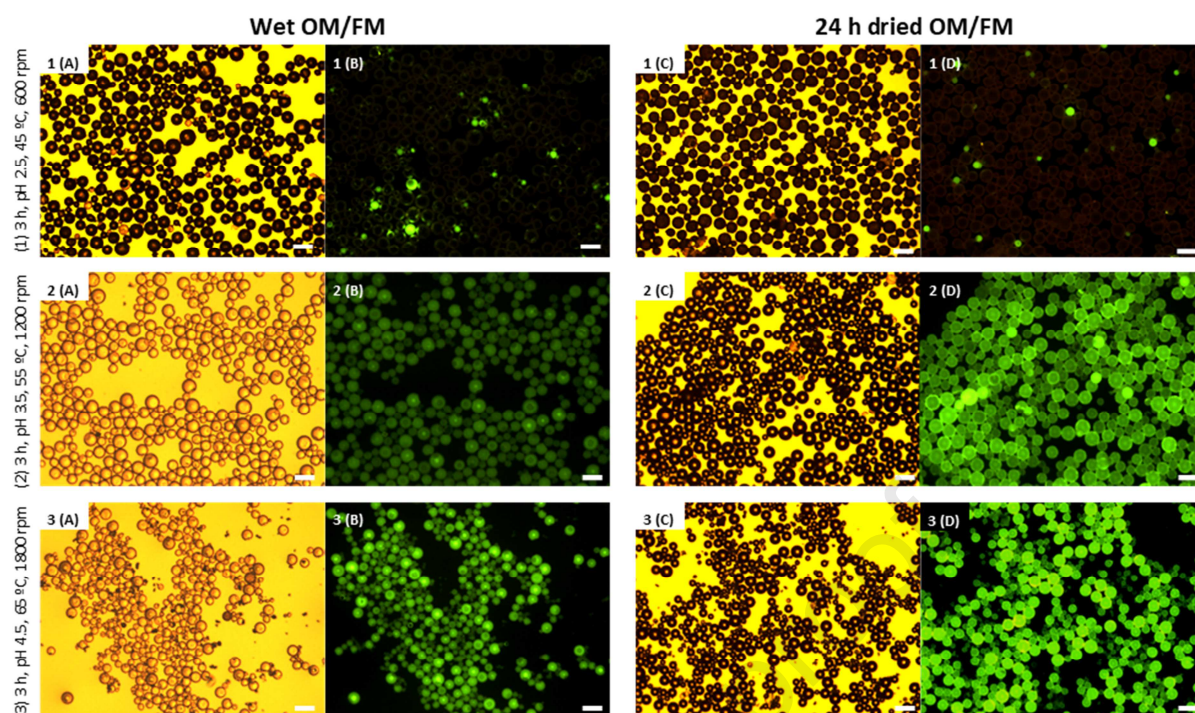


Figure 4. OM and FM images of set 1-3 microcapsules, dispersed in water and after a 24 h drying period (All scale bars are 100  $\mu\text{m}$ ).

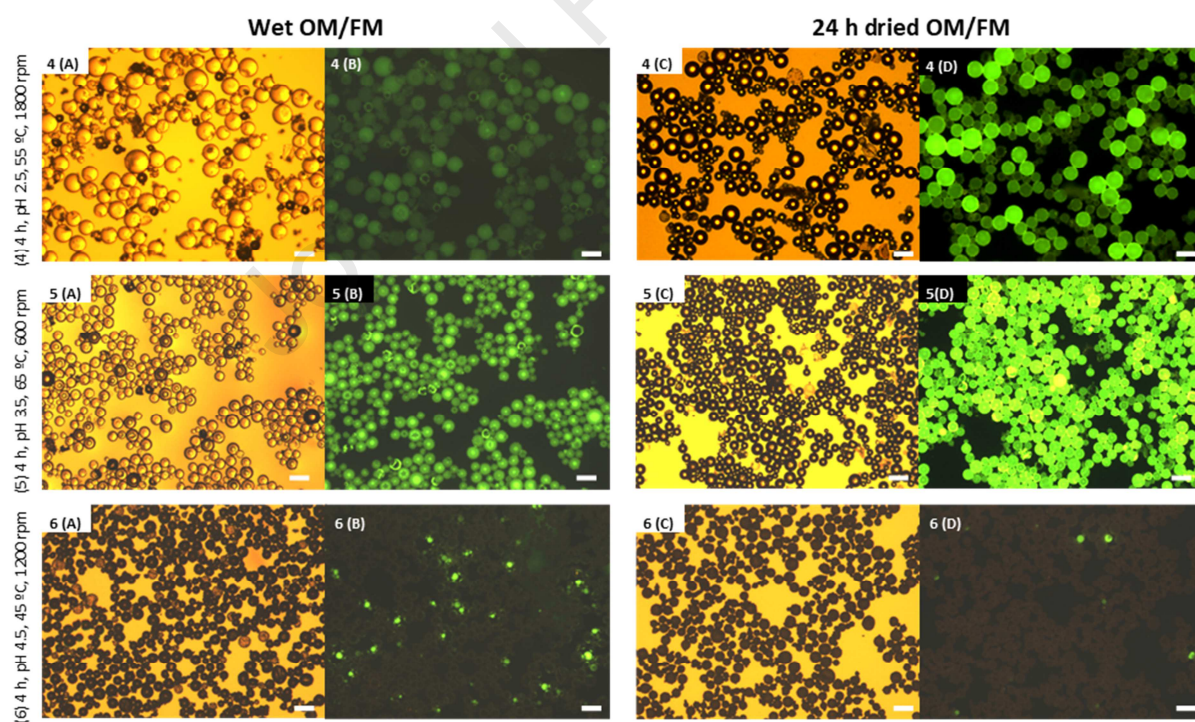


Figure 5. OM and FM images of set 4-6 microcapsules, dispersed in water and after a 24 h drying period (All scale bars are 100  $\mu\text{m}$ ).



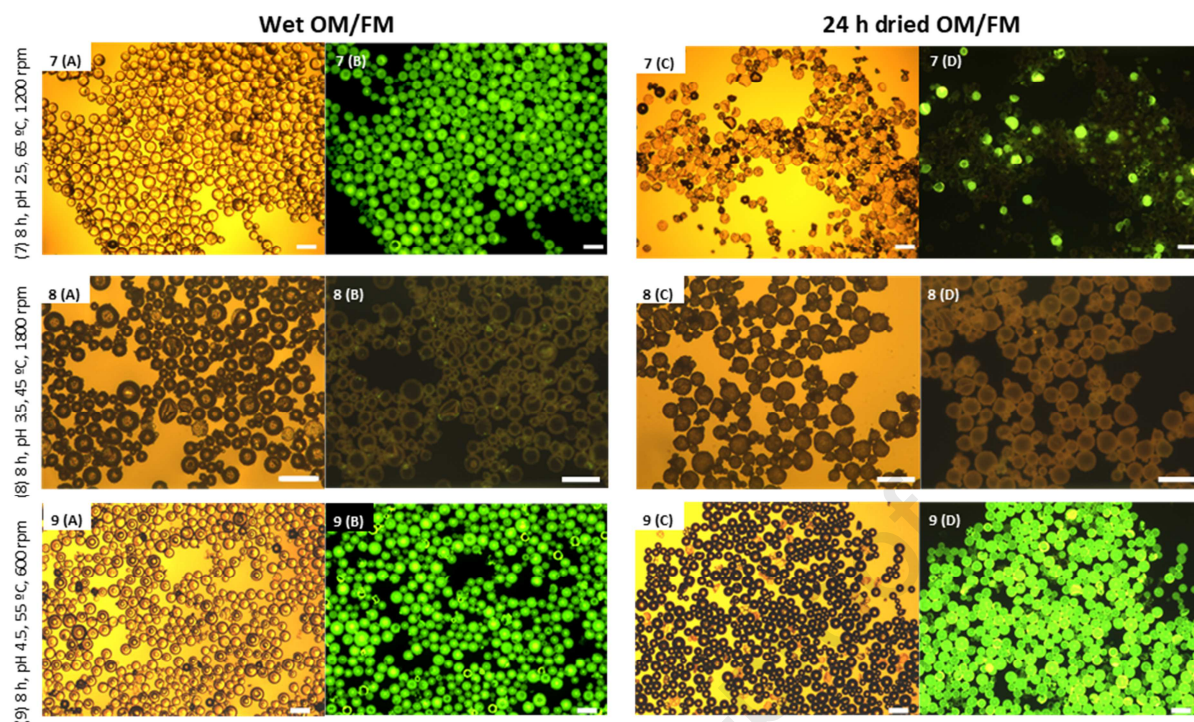


Figure 6. OM and FM images of set 7-9 microcapsules, dispersed in water and after a 24 h drying period (All scale bars are 100  $\mu\text{m}$ ).

As well as the OM and FM images to analyse core material retention, a 7-day payload analysis was carried out by observing the weight change over time, as shown in Figure 7. The results are in agreement with the OM and FM images, and all of the capsules prepared at 45  $^{\circ}\text{C}$  had very low retention, with set (1) having 17 % on the 7th day, set (6) having 13 %, and set (8) having 25 %. Furthermore, set (7) also had a low payload of 41 %, in agreement with the FM image 7(D) in Figure 6. There were 3 batches that had exceptionally high payloads above 90 %, which included set (2) obtaining 94 %, set (5) obtaining 96 % and set (9) obtaining 95 % after the 7-day ambient drying period. However, reaction-set 2 was produced with the lowest reaction time of 3 hours, while reaction-set 5 and 9 were 4 and 8 hours respectively. In terms of time and cost saving, a 3- or 4-hour reaction time with excellent payload would be beneficial, while an 8-hour reaction would not provide any additional benefits in terms of payload in this case.

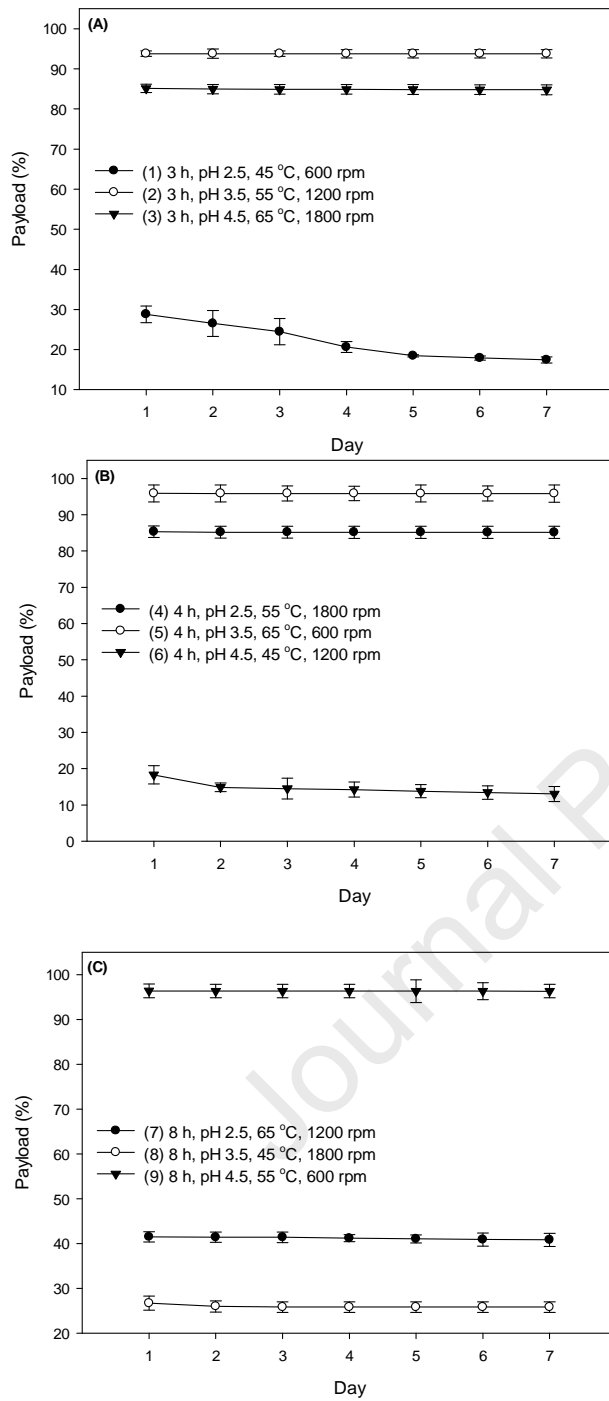


Figure 7. Payload measurements over a 7-day period for the 9 sets of formulated batches, with (a) 3 hour reaction, (b) 4 hour reaction and (c) 8 hour reaction.

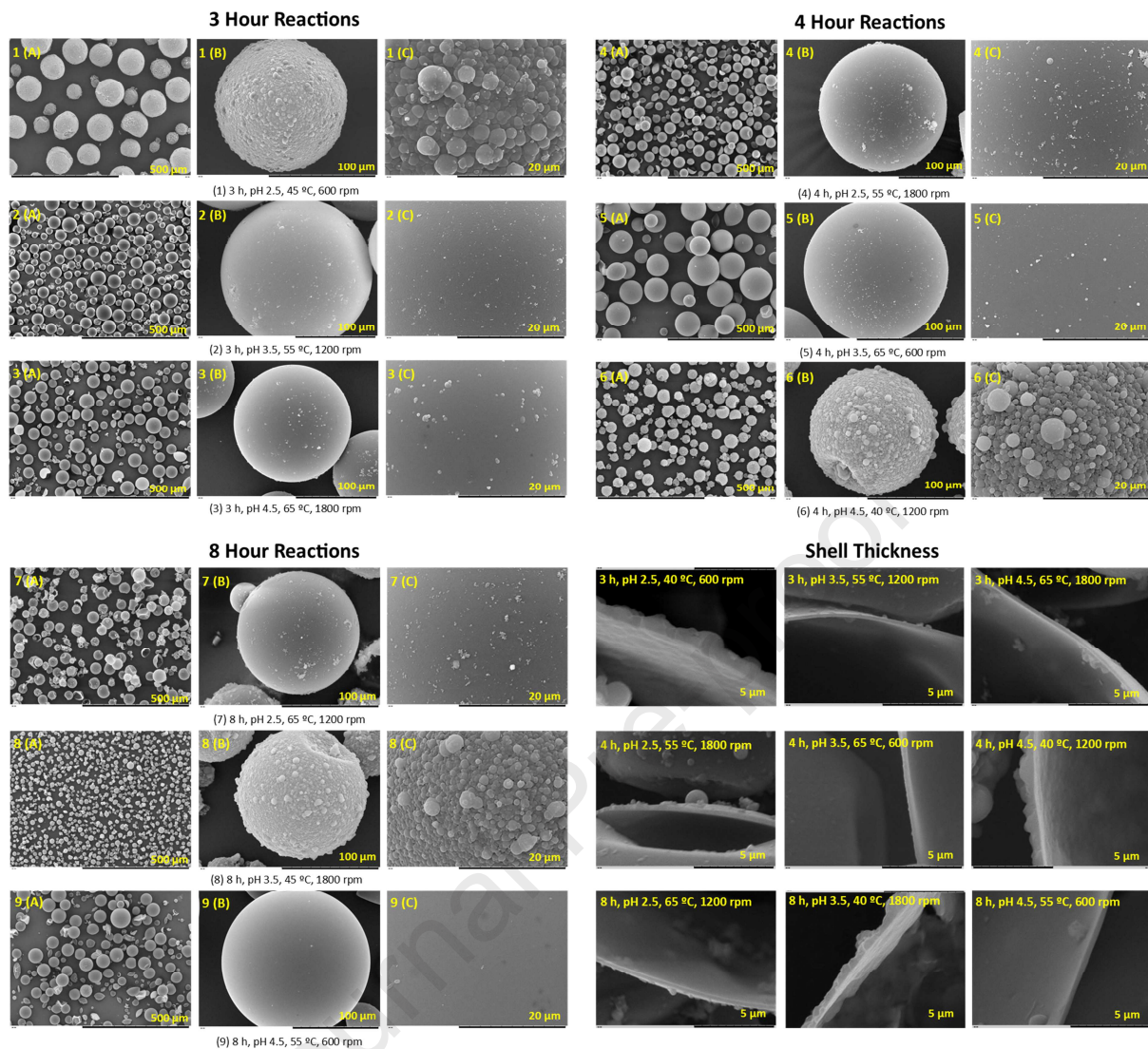


Figure 8. SEM micrographs of reaction sets 1-9 for the 3-hour, 4-hour and 8-hour reaction. For each set, the overall morphology, individual capsule and surface roughness is shown. Shell thickness micrographs for sets 1-9 also displayed.

Discerned in Figure 8 are the microcapsule SEM micrographs and shell thickness. All of the in situ polymerisation processes at 45 °C (sets 1, 6 and 8) produced much rougher microcapsules, as well as thicker shells. For example, reaction set 1 had a shell thickness of  $984 \pm 86$  nm, while reaction set 2 and 3 had shell thicknesses of  $255 \pm 19$  nm and  $217 \pm 14$  nm respectively. The UF particles formed at 45 °C engendered thick and rough shells, with poor coverage and high resultant porosity, which may contribute to the poor payload and high leakage of the microcapsules. It is also evident that the higher the temperature for the

microcapsules, the thinner the shells are observed to be. However, as deliberated, the prerogative over the kinetics of the reaction is also affected by the pH of the reaction, which can also affect the surface roughness. It is onerous to discern whether reaction time had much of an effect on the shell thickness, due to the synergistic properties of the multi-component factorial experimental conditions.

S/N ratio plots were then plotted for each process parameter studied; (a) the reaction time, (b) the pH, (c) the reaction temperature and (d) the homogenization speed, as conveyed in Figure 9. As the aim of this work was to maximise the response, the higher the S/N ratio, the more significant that parameter was at reducing the noise factors. Taking into account of the 9 orthogonal arrays, it can be seen that 3 hours reaction time had the highest S/N ratio. A pH of 3.5 was calculated to have the highest S/N ratio, followed by a stirring speed of 1200 rpm, as well as a temperature of 55 °C. Therefore, the most efficient combination of process parameters is 3 h, pH 3.5, 55 °C and 1200 rpm. Customarily, a confirmation experiment is required for these specific parameters to evaluate the individual S/N ratios for the payload, yield, and encapsulation efficiency, however, it is expedient that reaction run number 3 has these exact parameters, as shown in Table 3. With these results, it is evident that 3 hours reaction time is sufficient to create capsules with excellent core material content and retention.

The study carried out by Brown et al. [9] for the formulation of dicyclopentadiene microcapsules had process parameters of 4 h, pH 3.5, 55 °C, and various stirring speeds from 200 – 2000 RPM. Other examples of the formulation processes being maintained for 4 hours include Ullah et al. [38], Bolimowski et al. [39] and Zhang et al. [40]. However, this study has shown that conceivably 3 hours would have been sufficient for the reaction time, for a more volatile core material, which would result in saving of time and cost.



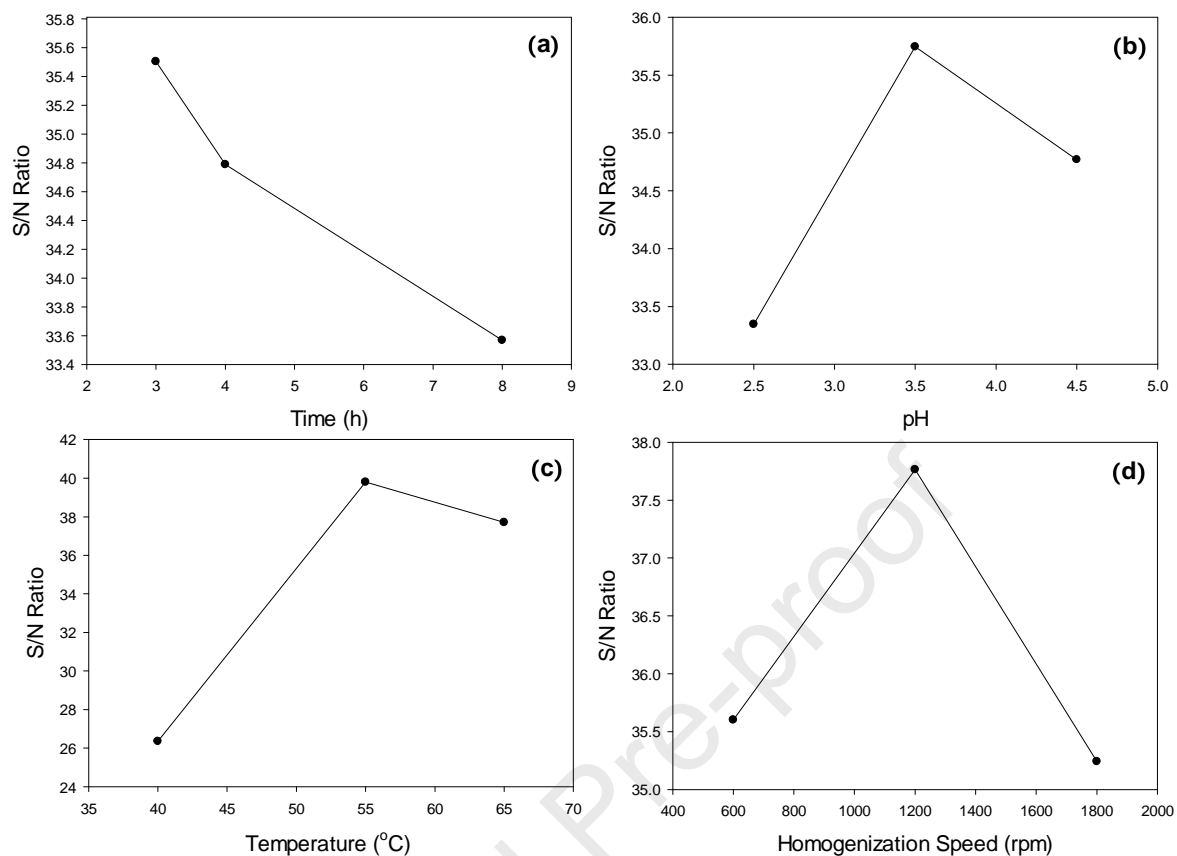


Figure 9. S/N ratio plots for the effects of process parameters on (a) the reaction time, (b) the pH, (c) the reaction temperature and (d) the homogenisation speed.

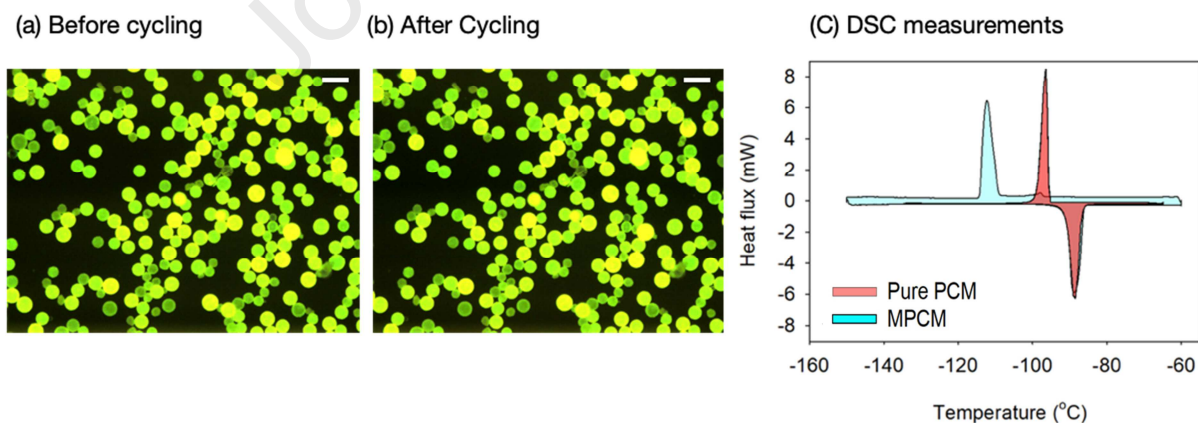


Figure 10. (a) FM images of microcapsules before and (b) after thermal cycling (10 cycles) (Scale bars are 100  $\mu\text{m}$ ). (c) DSC measurements of pure heptane PCM and the microencapsulated PCM with the reaction conditions of 3 h, pH 3.5, 55 °C and 1200 rpm.

The thermostability of MPCS is a pivotal factor to ensure the successful utilization in latent heat energy storage systems. Subsequently, by measuring the thermo-physical properties of the PCMs, thermal stability of PCMs can be established. Thermal cycling of the PCMs was then carried out with the microcapsules produced with the most efficient parameters (3 h, pH 3.5, 55 °C and 1200 rpm) and the results are seen in Figure 10 (a) and (b). It is observed that the FM images before and after cycling showed very little differences after 10 cycles, as the bright green-fluorescent colour and shape integrity of the microcapsules were maintained.

As seen in figure 10 (C), the melting point of the encapsulated batch was  $-113$  °C, and a melting point of  $-89$  °C, compared to pure heptane sample with a freezing and melting point of  $-93$  °C and  $-89$  °C degrees respectfully. The latent heat for the MPCM sample was calculated to 99.8 J/g via the integration of the DSC data. This is comparable to various other studies in which PUF-paraffin microcapsules formulated via in situ polymerization had latent heat values of 74.2 J/g [41], 47.7 J/g [42] and poly(melamine-formaldehyde) (PMF)-paraffin microcapsules with values of 102.9 J/g and 90.8 J/g [43].

### 3.3. ANOVA analysis of variance

Analysis of Variance (ANOVA) is a statistical model that is utilised to evaluate the mean response magnitude (% contribution) for each parameter in the orthogonal experiments [44]. The influence of each experimental factor with respect to the payload, yield, and the encapsulation efficiency was determined by one-way ANOVA analysis. In this analysis, the sum of the squares (total variation) is equal to the sum of the squares of deviation for all of the experimental parameters and the error components (e.g. adding the variation for each experimental factor). The following equations were used for the ANOVA analysis:

$$SS_T = SS_P + SS_Y + SS_{EE} \quad (5)$$

$$SS_T = \sum_1^n y_i^2 - \frac{G^2}{n} \quad (6)$$

$$SS_k = \sum_{i=1}^t \left( \frac{Sy_i^2}{t} \right) - \frac{G^2}{n} \quad (7)$$

where  $SS_T$  is the total sum of squares,  $SS_P$  is the sum of squares of the payload,  $SS_Y$  is the sum of squares of the yield,  $SS_{EE}$  is the sum of squares of the encapsulation efficiency,  $n$  is the number of repeats,  $Sy_i^2$  is the sum of all the trials involving parameter  $k$  at level  $i$ , and  $G$  is the resultant data for all the trial runs.

One-way ANOVA analysis was carried out for the payload, encapsulation efficiency and the yield, as conveyed in Table 5, Table 6, and Table 7. For the payload, it is observed that temperature had the highest contribution, followed by homogenization speed, pH, and time. It was expected that temperature would have a large effect on this factor, as observed in section 3.2, capsules produced at 45 °C did not survive ambient drying conditions. As the homogenization speed also affects the morphology and core content of the microcapsules, this is perhaps why it is the second most significant factor. For the yield, as seen in Table 6, temperature again is the most significant factor, followed by pH, reaction time and homogenization speed. Again, temperature is observed to be the most significant parameter in this case. For the encapsulation efficiency, as conveyed in Table 7 temperature again is the most imperative parameter, followed by pH, reaction time and homogenization speed.

Figure 11 illustratively conveys the percentage contributions on the radar graphs for the payload (a), yield (b) and encapsulation efficiency (c), as well as the combined overall contribution for the payload, yield, and encapsulation efficiency. The combined bar chart has very consistent overall results, exhibiting that temperature is the main determinant, with a value of about 83.1 % contribution, followed by pH at 6.8 %, proceeded by reaction time at 5.2 %, and finally a homogenization speed contribution of 4.9 %.

Overall, it is very clear that temperature is the main governing factor in these reactions, which is in agreement with the results observed in Table 4. This has ultimately shown the key considerations when designing experimental conditions for in situ polymerization processes.

Table 5. ANOVA for the microcapsule payloads

Payload - Analysis of variance				
Source	Degree of Freedom	Sum of Squares	Variance	Percentage Contribution
Time	2	479.8	239.9	5.0
pH	2	597.8	298.9	6.2
Temp	2	7670.1	3835.0	79.9
H. Speed	2	849.6	424.8	8.9
Error	0	0	0	0
Total	8	9597.3	4798.6	100.0

Table 6. ANOVA for the microcapsule yield

Yield - Analysis of variance				
Source	Degree of Freedom	Sum of Squares	Variance	Percentage Contribution
Time	2	43.9	22.0	7.9
pH	2	48.7	24.4	8.8
Temp	2	442.1	221.1	79.9
H. Speed	2	18.4	9.2	3.4
Error	0	0	0	0
Total	8	553.2	276.7	100.0

Table 7. ANOVA for the microcapsule encapsulation efficiency

Encapsulation Efficiency - Analysis of variance				
Source	Degree of Freedom	Sum of Squares	Variance	Percentage Contribution
Time	2	144.6	91.5	2.7
pH	2	291.2	183.5	5.3
Temp	2	5866	3087.9	89.5
H. Speed	2	259.2	86.4	2.5
Error	0	0	0	0
Total	8	6561	3449.4	100.0

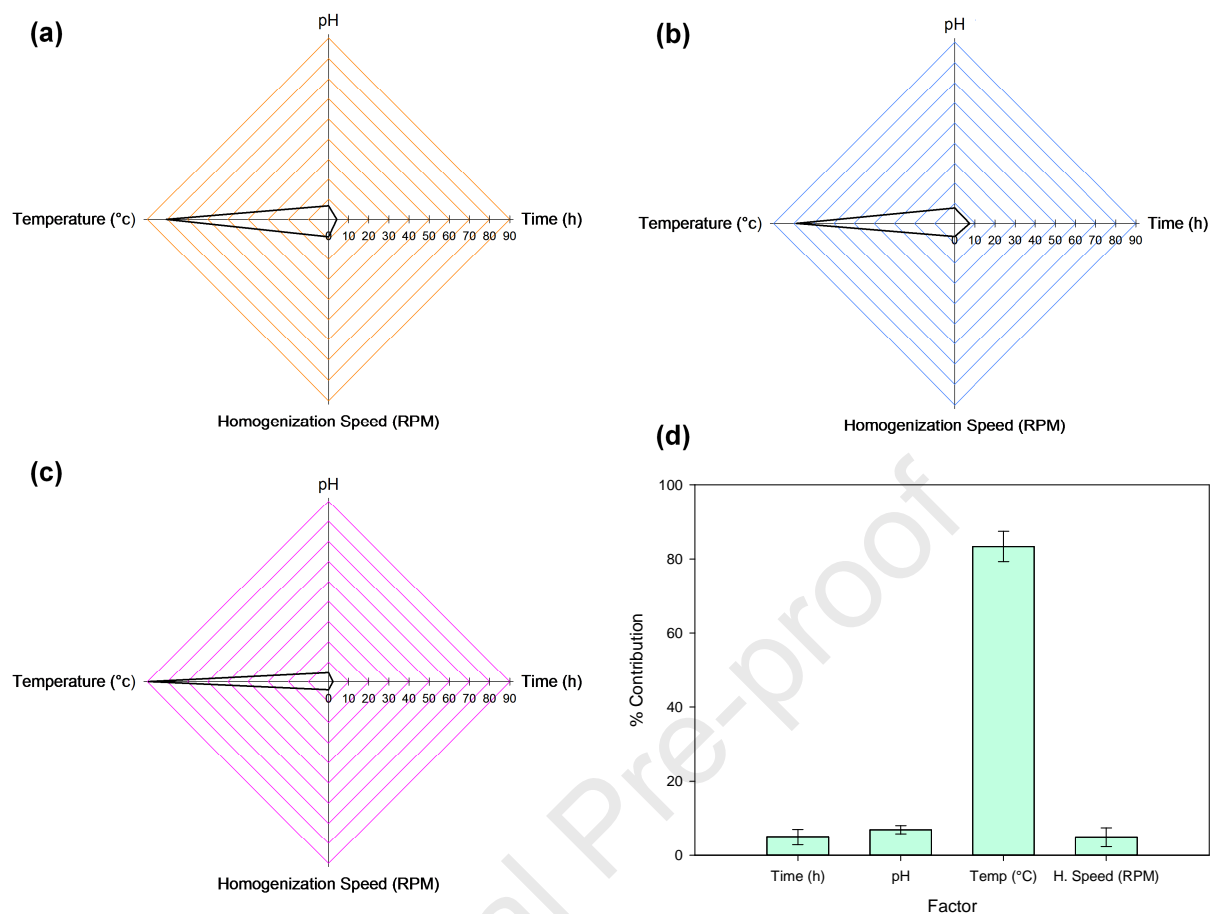


Figure 11. Radar graphs conveying the percentage contributions of the process conditions on (a) the payload, (b) the yield (c) the encapsulation efficiency; (d) the combination of all the contributions.

#### 4. Conclusions

In this work, the Taguchi orthogonal experimental design was used to study the process optimisation of PUF microcapsules containing a core of volatile heptane paraffin as PCM. The influences of experimental parameters of reaction time, pH, temperature and homogenization speed were all examined. The S/N ratio plots for the four parameters conveyed the most efficient combination: 3 h, pH 3.5, 55 °C and 1200 rpm. Systematically, it was observed that capsules with exceptional payload (95.2 %) long-term core material retention and thermal stability were produced. Such findings convey the significance of this work, with many researchers utilising 4 h and longer reaction times for less volatile core

materials, as well as higher temperatures for the formulation process, which is superfluously more timely and costly. The ANOVA analysis presented an insightful observation into the parameters that had the most governing effects of the process. It was observed that temperature had the highest effect, and microcapsules were not formed under 45 °C.

### Acknowledgements

The authors express their sincere gratitude to the Engineering and Physical Sciences Research Council (EPSRC) for the funding provided to this project (EP/N000714/1 and EP/N021142/1).

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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